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The objective of this work was to synthesize and study early-transition-metal silyl compounds that have the potential to carry out novel chemical transformations and to serve as precursors to solid-state materials containing both silicon and an early-transition-metal. Previously this field was quite undeveloped, therefore we surveyed a number of approaches to the synthesis of these new M-Si bonded species.

In the period of this grant, we discovered several routes to new early-transition-metal silyl complexes. These complexes contain $-SiMe_3$, $-Si(SiMe_3)_3$ and $-SiHMes_2$ (Mes = mesityl) silyl groups. The new complexes, of scandium, zirconium, hafnium, niobium and tantalum, have been characterized by a variety of spectroscopic techniques, including X-ray crystallography. Reactivity studies with these new complexes establish basic reactivity patterns toward a range of reactants. Unusual reactions that were discovered for these M-Si bonds include: (1) reductive elimination fo silyl groups with chloride, (2) first observation of CO insertion into a transition-metal-silicon bond, (3) routes to the first stable formylsilane, $(Me_3Si)_3SiCHO$, (4) facile ether cleavage following CO/CO coupling by a tantalum-silicon bond, (5) formation of tetrahedral Lewis base adducts of $M(\eta^2-COSiR_3)$ silaacyl complexes, (6) insertion of organic carbonyls into a tantalum-silicon bond with nucleophilic silyl group transfer, and (7) facile photochemical and thermal insertions of ethylene into metal-silicon bonds.

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"Ether Cleavage Following Insertion of Carbon Monoxide into the Tantalum-Silicon Bond of $(\eta^5$-$C_5Me_5)Ta(SiMe_3)Cl_3$," J Arnold and T D Tilley, *J Am Chem Soc, 107,* 6409 (1985)

"Tetrahedral Lewis Base Adducts of an Acyl. Preparation and X-ray Structure of the Pyridine Adduct $(\eta^5$-$C_5Me_5)Cl_3Ta[\eta^2$-$OC(SiMe_3)(NC_5H_5)]$," J Arnold, T D Tilley and A L Rheingold, *J Am Chem Soc, 108,* 5355 (1986)

"Preparation and Reaction Chemistry of Trimethylsilyl Derivatives of Tantalum. X-ray Structures of d^0 $(\eta^5$-$C_5Me_5)Ta(SiMe_3)Cl_3$ and d^1 $(\eta^5$-$C_5Me_5)Ta(SiMe_3)(PMe_3)Cl_2$," J Arnold, D N Shina, T D Tilley and A M Arif, *Organometallics, 5,* 2037 (1986)

"Coordinatively Unsaturated Tris(trimethylsilyl)silyl Complexes of Chromium, Manganese and Iron," D M Roddick, T D Tilley, A L Rheingold and S J Geib, *J Am Chem Soc, 109,* 945 (1987)

"Preparation and Reaction Chemistry of Trimethylsilyl Derivatives of Niobium. Redox Chemistry of $(\eta^5$-$C_5H_5)_2Nb(SiMe_3)Cl$ and X-ray Structures of $(\eta^5$-$C_5H_5)_2Nb(SiMe_3)(\eta^2$-$C_2H_4)$ and $[(\eta^5$-$C_5H_5)_2Nb(CH_2SiMe_3)Cl]PF_6$," J Arnold, T D Tilley, A L Rheingold and S J Geib, *Organometallics, 6,* 473 (1987)

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Arnold and T D Tilley, *J Am Chem Soc, 109,* 3318 (1987)

"Formation of the Novel Benzophenone Sila-acylhydrazonato Complex (η^5-C$_5$Me$_5$)Cl$_3$Ta-[OC(SiMe$_3$)NNCPh$_2$] Following Addition of Diphenyldiazomethane to an η^2-Sila-acyl Ligand," J Arnold, T D Tilley, A L Rheingold and S J Geib, *J Chem Soc, Chem Commun,* 793 (1987)

"Preparation and Characterization of Tris(trimethylsilyl)silyl Derivatives of Zinc, Cadmium and Mercury. X-ray Crystal Structure of Zn[Si(SiMe$_3$)$_3$]$_2$," J Arnold, T D Tilley, A L Rheingold and S J Geib, *Inorg Chem,* 26, 2106 (1987)

"An Arbuzov-like Reaction in the Trimethylphosphite-η^2-Silaacyl Adduct (η^5-C$_5$Me$_5$)Cl$_3$Ta{η^2-OC(SiMe$_3$)[P(OMe)$_3$]}," J Arnold, T D Tilley, A L Rheingold and S J Geib, *Inorg Chem, 26,* 2556 (1987)

"Preparation, Characterization and X-ray Crystal Structure of an Acetonitrile-Complexed Ruthenium Silylene," D A Straus, T D Tilley, A L Rheingold and S J Geib, *J Am Chem Soc, 109,* 5872 (1987)

"Preparation of the First Stable Formylsilane, (Me$_3$Si)$_3$SiCHO, from a Zirconium η^2-Silaacyl Complex," F H Elsner, H-G Woo and T D Tilley, *J Am Chem Soc, 110,* 313 (1988)

"Dimesitylsilyl Derivatives of Zirconium," D M Roddick, R H Heyn and T D Tilley, *Organometallics,* in press

"Reaction of an Early Transition-Metal η^2-Silaacyl Complex with Pyridine. Diastereoselectivity in the Formation of a (2-Pyridyl)(silyl)methoxy Ligand," J Arnold, H-G Woo, T D Tilley, A L Rheingold and S J Geib, *Organometallics,* in press

"Carbonylation Chemistry of the Tantalum Silyl (η^5-C$_5$Me$_5$)Cl$_3$TaSiMe$_3$. Synthesis, Characterization, and Reaction Chemistry of (η^5-C$_5$Me$_5$)Cl$_3$Ta(η^2-COSiMe$_3$) and Derivatives," J Arnold, T D Tilley, A L Rheingold, S J Geib and A M Arif, *J Am Chem Soc,* in press

"Reactions of (η^5-C$_5$H$_5$)(η^5-C$_5$Me$_5$)Zr[Si(SiMe$_3$)$_3$]X (X = Cl, Me) Complexes with Carbon Monoxide and the Isocyanide 2,6-Me$_2$C$_6$H$_3$NC. Crystal Structure of (η^5-C$_5$H$_5$)(η^5-C$_5$Me$_5$)Zr[η^2-C(N-2,6-Me$_2$C$_6$H$_3$)Si(SiMe$_3$)$_3$]Cl," F H Elsner, T D Tilley, A L Rheingold and S J Geib, *J Organomet Chem,* in press

"Preparation and Characterization of Tris(trimethylsilyl)silyl and Tris(trimethylsilyl)germyl Derivatives of Zirconium and Hafnium. X-ray Crystal Structures of (η^5-C$_5$Me$_5$)Cl$_2$HfSi(SiMe$_3$)$_3$ and (η^5-C$_5$Me$_5$)Cl$_2$HfGe(SiMe$_3$)$_3$," J Arnold, D M Roddick, T D Tilley, A L Rheingold and S J Geib, *Inorg Chem,* in press

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this work was to synthesize and study early-transition-metal silyl compounds that have the potential to carry out novel chemical transformations and to serve as precursors to solid-state materials containing both silicon and an early-transition-metal. Previously this field was quite undeveloped, therefore we surveyed a number of approaches to the synthesis of these new M-Si bonded species.

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Final Technical Report (Grant No. AFOSR-85-0228)

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The early-transition-metals and silicon are principle components of a number of materials with interesting structural and electronic properties.[1] Examples include transition-metal silicates and silicides, which are refractory materials that have applications as electronic components, structural materials and oxidation-resistant coatings. Use of organometallic precursors to such materials is an attractive approach, since the ceramic components are already chemically combined in well-defined stoichiometries at the molecular level. Unfortunately, very few compounds containing both an early-transition-metal and silicon are known. We have been investigating this area by examining approaches to the synthesis of early-metal silicon derivatives.

In 1985, our proposal to develop routes to early-transition-metal silyl compounds and *investigate their chemical properties was funded by AFOSR.* Previously this field was quite undeveloped - the only well-characterized Zr and Hf silyls were the complexes $Cp_2M(SiPh_3)Cl$ (M = Zr, Hf; $Cp = \eta^5-C_5H_5$),[2] which had not been studied in detail, and the first reports of Nb and Ta silyls, describing $Cp_2M(SiMe_2Ph)H_2$ (M = Nb, Ta), appeared in early 1985.[3] A more in-depth study of early-transition-metal silyl compounds seemed timely, given their potential to carry out novel chemical transformations and the current interest in materials containing both silicon and an early-transition-metal. In this grant period, we have discovered routes to a number of early-transition-metal silyl complexes, and have investigated their fundamental physical and chemical properties. These M-Si bonded species have proven to have a rich reaction chemistry. Many of the goals set forth in the original proposal to AFOSR have been accomplished, and this work has provided the first useful systems for investigating structure, bonding and reactivity in early-transition-metal silyl compounds.

Synthesis and Properties of New Silyl Complexes

Summarized below are some of the major results that we have obtained from our work in early-transition-metal silicon chemistry. The key to our initial investigations in this area, and the most significant challenge for further development, is the discovery of preparative routes to early-transition-metal-silicon bonded compounds. So far, the most versatile route involves displacement of halide anion from the metal by a silyl anion. This method is therefore somewhat limited due to the availability of suitable silyl anion sources. In our studies we have successfully employed the reagents $Al(SiMe_3)_3 \cdot OEt_2$,[4] $Hg(SiMe_3)_2$,[5] $(THF)_3LiSi(SiMe_3)_3$,[6] and $(THF)_2LiSiHMes_2$ (Mes = mesityl)[7] to prepare new early metal silyls.

The aluminum reagent was used to prepare the crystalline Zr and Hf silyls **1** and **2**, which have proven to be convenient starting points for investigating the fundamental chemical properties of Zr-Si and Hf-Si bonds (eq 1, Cp = η^5-C_5H_5).[8] An X-ray crystal structure of a derivative of **1**,

$$Cp_2MCl_2 \quad + \quad Al(SiMe_3)_3 \cdot OEt_2 \quad \longrightarrow \quad \text{(structure)} \tag{1}$$

1, M = Zr
2, M = Hf

$Cp_2Zr(SiMe_3)(S_2CNEt_2)$, revealed a surprisingly long Zr-Si bond length of 2.815 (1) Å.

In a similar manner, the green tantalum silyl $Cp^*Ta(SiMe_3)Cl_3$ (**3**) was prepared from Cp^*TaCl_4 and $Al(SiMe_3)_3 \cdot OEt_2$. Compound **3** has been completely characterized by a number of techniques, including X-ray crystallography (Figure 1). This electron deficient, highly reactive complex exhibits an unusual ^{29}Si NMR chemical shift, 122.9 ppm, by far the most downfield-shifted ^{29}Si NMR resonance known for a mononuclear silyl derivative. From reaction of the d^0 complex **3** with reducing agents, we have also obtained the red, paramagnetic, d^1 complex $Cp^*Ta(SiMe_3)(PMe_3)Cl_2$ (**4**, Figure 2) and the d^2 compound $CpCp^*Ta(SiMe_3)Cl$ (**5**).[9]
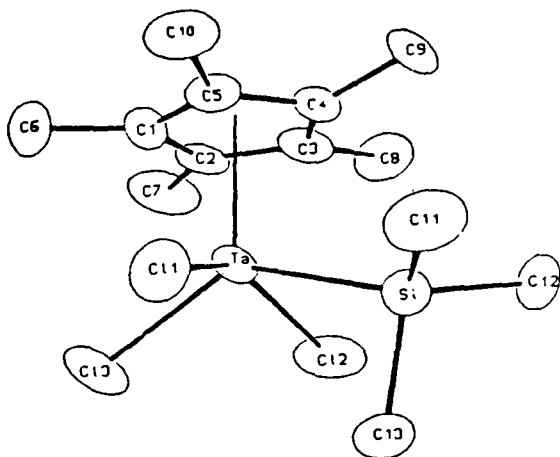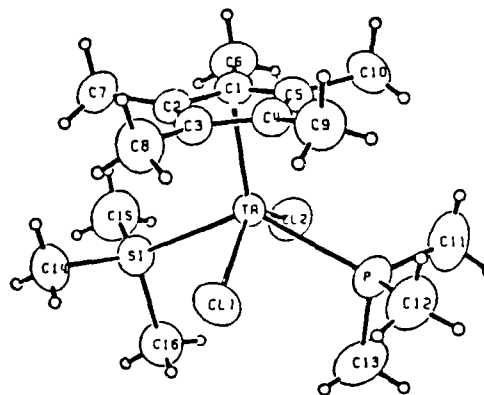
Figure 1. ORTEP view of **3**.

Figure 2. ORTEP view of **4**.

Structural data for late or low-valent transition-metal silyl derivatives show that metal-silicon distances are shorter than expected for a single covalent bond. This has been attributed to π-bonding involving donation of d-electron density from the transition-metal to silicon. The d^0 silyl complexes $Cp_2Zr(SiPh_3)Cl$ and $Cp_2Zr(SiMe_3)S_2CNEt_2$, for which such π-bonding is not possible, actually have Zr-Si bond lengths somewhat longer than expected based on covalent radii. The latter trend is apparently not general for d^0 silyls, since $Cp_2Ta(SiMe_2Ph)H_2$ contains a "normal" Ta-Si single bond distance (2.651(4) Å). The isolation of tantalum(IV) and tantalum(V) silyl complexes with very similar coordination geometries presented the opportunity to examine the effect of d^n configuration on the metal-silicon bond length.[9]
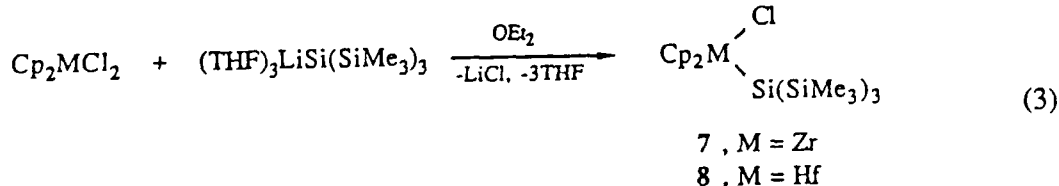
The Ta-Si bond length in d^0 complex **3** (2.669(4) Å) is somewhat longer than that found for the d^1 complex **4** (2.642(1) Å) despite the fact that the covalent radius of the tantalum(IV) center should be greater than that of the tantalum(V) center in **3**. This reduction in bond length of *ca.* 0.03 Å per d-electron may reflect some degree of π-bonding between the Si and Ta in **4**. A similar effect has been observed for metal-phosphine bonding. The predicted single covalent bond distances calculated from covalent radii are 2.47 and 2.53 Å for **3** and **4**, respectively. Though the *differences in steric and electronic effects* in **3** and **4** introduce some error, it therefore appears that both Ta-Si bonds are somewhat elongated, by 0.20 Å in **3** and 0.11 Å in **4**.[9]

Only one previous report briefly describes a well-characterized niobium silyl compound.[3] We have obtained the purple, paramagnetic (d^1) niobium silyl $Cp_2Nb(SiMe_3)Cl$ (**6**) by reaction of Cp_2NbCl_2 with $Hg(SiMe_3)_2$ in refluxing benzene (eq 2). Cyclic voltammetry studies in

$$Cp_2NbCl_2 + Hg(SiMe_3)_2 \xrightarrow[\text{4 h}]{C_6H_6, \text{ reflux}} Cp_2Nb(SiMe_3)Cl + Me_3SiCl + Hg \quad (2)$$
$$\mathbf{6}$$
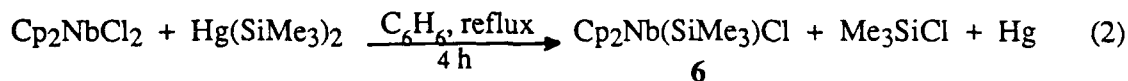
tetrahydrofuran show that reduction of 17-electron **6** is reversible with $E_{1/2} = 2.05$ V. In contrast, oxidation of **6** is irreversible. Consistent with the electrochemical studies, **6** is reduced by Na/Hg in the presence of suitable donor ligands to give stable niobium(III) silyls $Cp_2Nb(SiMe_3)(L)$ (L = CO, PMe_3, C_2H_4). The ethylene complex $Cp_2Nb(SiMe_3)(\eta^2\text{-}C_2H_4)$ has been characterized by X-ray crystallography. Chemical oxidation of **6** appears to generate the highly reactive, cationic niobium(V) silyl $[Cp_2Nb(SiMe_3)Cl]^+$ (vide infra).[10]

The silyl lithium $(THF)_3LiSi(SiMe_3)_3$ appears to be a more versatile reagent for the preparation of zirconium and hafnium silyl derivatives. By methods analogous to those used to obtain **1** and **2**, pentane-soluble **7** and **8** are prepared in *ca.* 70% yield (eq 3). The oxo-bridged

$$Cp_2MCl_2 + (THF)_3LiSi(SiMe_3)_3 \xrightarrow[\text{-LiCl, -3THF}]{OEt_2} Cp_2M\begin{smallmatrix} Cl \\ Si(SiMe_3)_3 \end{smallmatrix} \quad (3)$$

$$\mathbf{7}, M = Zr$$
$$\mathbf{8}, M = Hf$$

binuclear silyl $Cp_2(Cl)Zr(\mu\text{-}O)ZrCp_2[Si(SiMe_3)_3]$ can be prepared in a similar fashion. Reaction of $(THF)_3.LiSi(SiMe_3)_3$ with **1** affords the bis(silyl) $Cp_2Zr[Si(SiMe_3)_3](SiMe_3)$, which crystallizes from pentane as intensely-colored red prisms.[11]

In our search for early metal silyl complexes that exhibit new types of structures and new reactivity patterns, we have discovered mono-ring complexes of zirconium and hafnium (**9** and **10**, eq 4).[12] The hafnium derivative **10** has been structurally characterized. By analogous

$$Cp^*MCl_3 + (THF)_3LiSi(SiMe_3)_3 \xrightarrow[\text{-LiCl, -3THF}]{OEt_2} \quad (4)$$

$$\mathbf{9}, M = Zr$$
$$\mathbf{10}, M = Hf$$
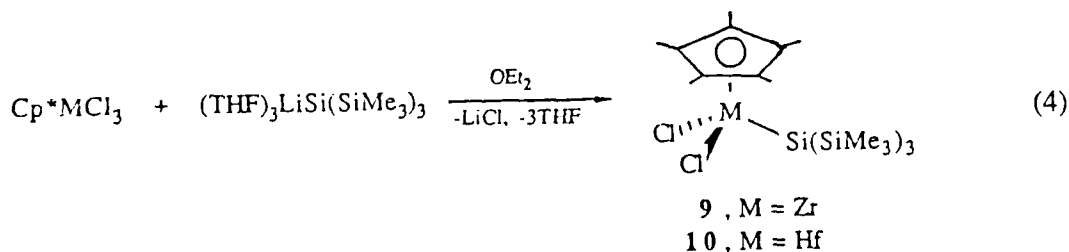
procedures, we have also recently obtained the first zirconium silyl that does not contain a cyclopentadienyl ancillary ligand, $({}^tBuO)_3ZrSi(SiMe_3)_3$ (**11**). X-ray crystallography shows that in

the solid state the latter compound exists in the gauche conformation.[13]

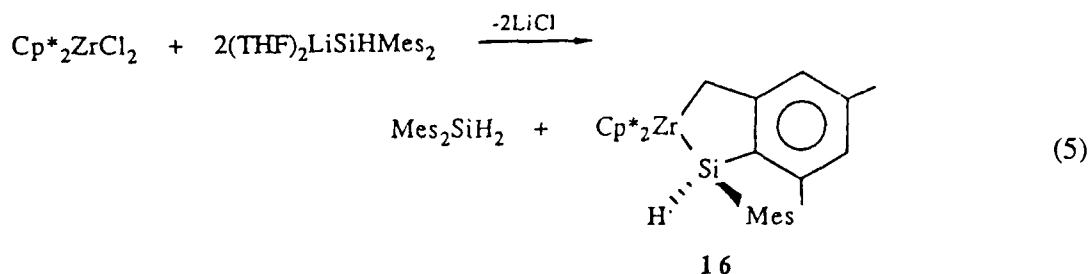Lately, the above method has been employed to prepare the first example of a scandium silyl, $Cp_2Sc[Si(SiMe_3)_3](THF)$ (12), from reaction of $[Cp_2ScCl]_2$ with $(THF)_3LiSi(SiMe_3)_3$. As described below, in some respects 12 is the most reactive early-transition-metal-silicon bond that we have yet discovered. This is consistent with the very long Sc-Si distance in 12, 2.86(1).[14]

Many of the silyl systems described above may be functionalized via chloride displacement reactions to provide new mixed-ligand silyl complexes. In this way, we have obtained the mixed alkyl silyls $Cp_2Zr(SiR_3)R'$ (R = Me, $SiMe_3$; R' = Me, CH_2CMe_3, CH_2SiMe_3)[15] and $Cp^*Ta(SiMe_3)Me_3$,[9] and borohydride derivatives $Cp_2Zr(SiR_3)BH_4$ (R = Me, $SiMe_3$).[8,11] These compounds are of interest since they allow investigations into the effects of different functional groups on silyl bonding and reactivity (vide infra).

Given the limited range of silyl anion reagents for preparation of early metal silyl complexes, and in particular the scarcity of ones containing Si-H bonds, we have attempted to prepare stable, isolable derivatives of the type $MSiHR_2$ (M = an alkali metal). One success is isolation of the lithium silyl $(THF)_2LiSiHMes_2$ (13), prepared from Mes_2SiHCl and lithium powder in tetrahydrofuran. Generation of 13 in solution was previously reported by Weidenbruch.[15a] The $^1J_{SiH}$ coupling constant (101 Hz) and the $\nu(Si-H)$ infrared stretching frequency (1910 cm^{-1}) for 13 are consistent with a very electropositive substituent at silicon.[7]

Zirconium silyls $Cp'_2Zr(SiHMes)Me$ (14, $Cp' = \eta^5-C_5H_5$; 15, $Cp' = \eta^5-C_5Me_5$) are readily obtained upon reaction of the chlorides $Cp'_2Zr(Me)X$ (X = halide) with 13. Again, spectroscopic properties associated with the Si-H bonds suggest the presence of an electropositive substituent at silicon (for 15, $^1J_{SiH}$ = 142 Hz; $\nu(Si-H)$ = 2060 cm^{-1}). Compound 15 appears to be quite sterically congested, since restricted rotation about both Si-C(Mes) ($\Delta G^{\ddagger}$ = 10.4 ± 0.2 kcal mol^{-1}) and Zr-Si($\Delta G^{\ddagger}$ = 11.8 ± 0.2 kcal mol^{-1}) bonds is observed. Use of 13 as a reagent for preparing metal silyls is somewhat limited. The presence of only one halide group in $Cp'_2Zr(Me)X$ seems to be important, since treatment of other metal chlorides (Cp^*HfCl_3, $ZrCl_4$, $HfCl_4$, $TaCl_5$, Cp^*TaCl_4, and $Cp^*_2ZrCl_2$) with 13 yielded no tractable metal silyl derivatives. In

every case, Mes_2SiH_2 was observed as the major silicon-containing product. An explanation for these results is suggested by the reaction of $Cp^*_2ZrCl_2$ with *two* equivalents of **13** (eq 5).

$$Cp^*_2ZrCl_2 \quad + \quad 2(THF)_2LiSiHMes_2 \quad \xrightarrow{\ -2LiCl\ }$$

$$Mes_2SiH_2 \quad + \quad Cp^*_2Zr \quad\quad\quad \quad\quad (5)$$

16

Apparently, the initially formed mono-silyl derivatives undergo rapid dehydrohalogenation reactions if metal-halogen bonds are present. This has been confirmed by the observation that $Cp^*_2Zr(SiHMes_2)Cl$, prepared by an alternate route, reacts with **13** to afford Mes_2SiH_2 and the metallacycle **16**.[7]
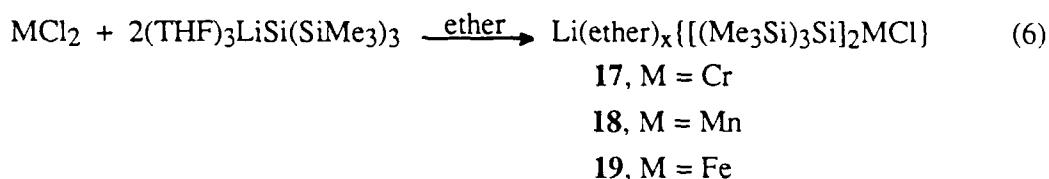
Most early-transition-metal silyl complexes that we have discovered are highly colored. This is an unusual property for d^0 metal compounds. The absorptions responsible for these colors are probably ligand-to-metal charge transfer transitions, and appear to play an important role in the photochemistry of some M-Si bonds.[16]

We have made numerous attempts to prepare other early metal silyls by the methods described above. In particular we have pursued simple binary silyls, $M(SiR_3)_n$, since these compounds are expected to possess a rich reaction chemistry and should serve as useful precursors to silicon-containing materials such as metal silicides, M_xSi_y. In some cases, treatment of a metal halide MCl_n with n equivalents of a silyl anion reagent results in reduction of the transition metal, possibly via electron transfer. Thus, milder silylating reagents may be required. In other cases, such as in the reaction between $TaCl_5$ and $Al(SiMe_3)_3 \cdot OEt_2$, the decomposition products R_3SiCl and R_3Si-SiR_3 are observed. The latter silicon-containing products may be the result of reductive elimination processes (vide infra). The aluminum reagent fails to react at all with many metal halides such as MCl_4 (M = Zr, Hf) and Cp^*MCl_3 (M = Zr, Hf), even under forcing conditions.

We have investigated the use of zinc, cadmium, and mercury silyls as milder reagents for the preparation of new transition metal silyls. As reagents for introducing the sterically hindered -

$Si(SiMe_3)_3$ ligand into the coordination sphere metals, the silyls $M[Si(SiMe_3)_3]_2$ (M = Zn, Cd, Hg) have been prepared from group 14 metal dihalides and $(THF)_3LiSi(SiMe_3)_3$. The crystal structure of the zinc derivative $Zn[Si(SiMe_3)_3]_2$ has been determined. We are presently investigating the utility of these new reagents.[17]

The large majority of transition-metal silyls are coordinatively saturated and contain CO, phosphines, or cyclopentadienyl ancillary ligands. Although we have so far been unable to obtain early metal silyls of the type $M(SiR_3)_n$, we have designed syntheses to closely related derivatives of other metals by use of sterically demanding silyl ligands. First-row transition-metal dichlorides react with 2 equivalents of $(THF)_3LiSi(SiMe_3)_3$ in ether solvents to afford air- and moisture-sensitive, anionic silyl complexes (eq 6).[18] Compounds 17-19 possess large magnetic moments

$$MCl_2 + 2(THF)_3LiSi(SiMe_3)_3 \xrightarrow{\text{ether}} Li(ether)_x\{[(Me_3Si)_3Si]_2MCl\} \quad (6)$$

17, M = Cr
18, M = Mn
19, M = Fe

consistent with high-spin electron configurations. Paramagnetic silyl complexes are quite rare, and did not previously exist for Cr, Mn or Fe. The crystal structure of $NEt_4\{[(Me_3Si)_3Si]_2FeCl\}$ reveals an unusual 3-coordinate geometry for the d^6 Fe(II) center (Figure 3). The chloride ligands
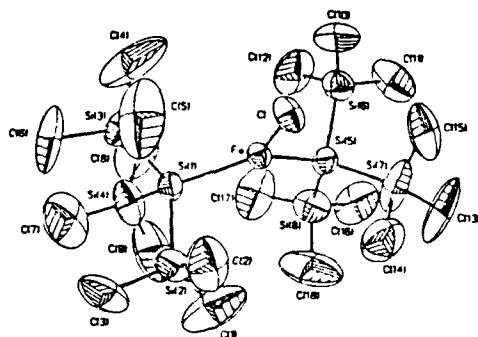

Figure 3. ORTEP drawing of $NEt_4\{[(Me_3Si)_3Si]_2FeCl\}$

in these complexes may be abstracted by electrophilic reagents, and in this way we have prepared $M[Si(SiMe_3)_3]_2 \cdot$ether (M = Mn, Fe; ether = OEt_2, 1,2-dimethoxyethane). Because these compounds contain only silyl and ether ligands (the latter should be weakly coordinated), it is of interest to evaluate their potential as precursors to metal silicide materials. Initial TGA experiments

with Fe[Si(SiMe$_3$)$_3$]$_2$·OEt$_2$ show that upon heating to 500°C, the compound gives a 41% "ceramic yield" of a material that by X-ray analysis appears to be a composite containing iron and silicon carbide.[19]

## Reactivity of Early-Transition-Metal Silyl Compounds

Research in this area has revealed a rich reaction chemistry that includes a number of processes unprecedented in transition-metal chemistry. The major results we have obtained in the early stages of our investigations of early transition-metal silyl chemistry are summarized below.

Basic Reactivity Patterns. Protic acids such as water cleave d^0 M-Si bonds in a manner that suggests a bond polarity of M$^+$-Si$^-$. For example, Cp$_2$Zr(SiMe$_3$)Cl (1) hydrolyzes cleanly to [Cp$_2$ZrCl]$_2$(μ-O) and HSiMe$_3$.[8] This reactivity is opposite to that generally observed for other (late) transition-metal silyls that have been studied.[20] Compound 1 also reacts rapidly with O$_2$ to give the siloxide Cp$_2$Zr(OSiMe$_3$)Cl, underscoring the importance of excluding air in preparations of early metal silyls.[8] The reactivity of an early-metal-silicon bond toward a nonpolar substrate was first observed in the reaction of 1 with H$_2$ to give [Cp$_2$ZrHCl]$_n$ and HSiMe$_3$.[11]

Intramolecular Competition Experiments. Mixed alkyl silyl complexes are being examined by mechanistic and chemical reactivity studies to compare M-Si bonds to the better-understood M-C bonds. Intramolecular competition experiments with Cp$_2$Zr(SiR$_3$)R′ compounds have shown that M-C bonds are preferentially cleaved by acids, suggesting greater bond polarity between the metal and carbon. Less polar reagents (e.g., H$_2$ and CO) can react preferentially with either Zr-C or Zr-Si bonds, depending on subtle steric and electronic factors in the alkyl silyl complex. Oxidizing agents (Ag$^+$, Cp$_2$Fe$^+$) preferentially cleave M-Si bonds, indicating that these M-Si bonds are weaker than comparable M-C bonds. Overall, these and other results suggest that M-C and M-Si bonds in these systems are more similar in reactivity than might have been predicted initially.[15]

Reductive Elimination of Silyl Groups with Chloride. Another unusual reaction discovered for early-transition-metal silyl species involves reductive elimination of a silyl group with chlorine.

These reactions have been observed in Ti, Nb and Ta complexes, and are induced by oxidation[10] or an incoming ligand.[9,11] Reductive elimination processes involving silyl ligands have received little attention, but are important steps in transition-metal-mediated reactions of silicon compounds (e.g., in Rochow's Direct Process[21] and hydrosilation catalysis[22]). These reactions appear to be clean, convenient methods for generation of low-valent complexes such as $Cp_2Ti(CO)_2$ and Cp^*TaCl_2(alkyne) (eq 7), or highly reactive intermediates such as $Cp^*TaCl_2(PMe_3)$ and $[Cp_2Nb]^+$.[9,10,11]

$$Cp^*Ta(SiMe_3)Cl_3 + \text{alkyne} \longrightarrow Cp^*TaCl_2(\text{alkyne}) + Me_3SiCl \qquad (7)$$
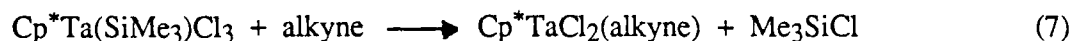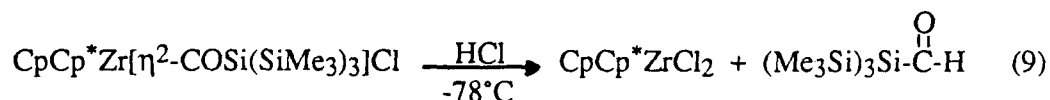
First Observation of CO Insertion into a Transition-Metal-Silicon Bond. Over the past 20 years, many attempts to carbonylate metal silyl derivatives, or observe migratory insertion of CO into a M-Si bond, have failed.[20] This situation contrasts sharply with the well-known CO insertion chemistry associated with transition-metal-carbon bonds. Carbon monoxide insertions into M-Si bonds were thought to be potentially useful in that they could provide new methods for CO activation, and perhaps provide new routes to acylsilanes, which are useful intermediates in organic synthesis. The first observation of CO insertion into a transition-metal-silicon bond was made in our laboratories (eq 8).[11,23] The silaacyl insertion product **20** was completely


$$\text{(8)}$$
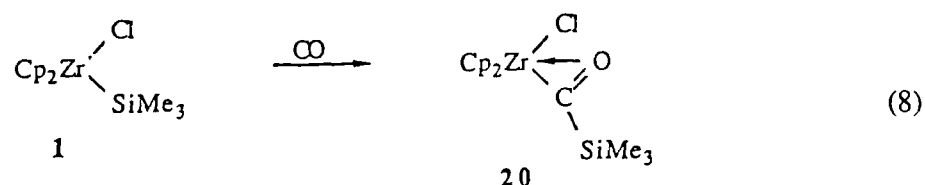
characterized by analytical and spectroscopic data, and by X-ray crystallography. We have now observed similar insertions in other early-transition-metal silyl compounds, and our investigations in this area have resulted in discovery of a number of surprising and unusual chemical reactions. Having discovered these new and potentially useful chemical systems, we extensively investigated their chemistry.

First Syntheses of Formylsilanes R₃SiCHO; New Preparations of Acylsilanes. Attempts to prepare formylsilanes (R_3SiCHO), dating back to 1947, led to the opinion that these species were unstable under a variety of conditions.[24] We have utilized transition-metal silaacyl derivatives as

intermediates in the preparations of the first examples of formylsilanes. Acidification of **20** by HCl at low temperature generates Me_3SiCHO, which is unstable above -25°C. The analogous reaction with $CpCp^*Zr[\eta^2\text{-}COSi(SiMe_3)_3]Cl$ provides the first stable, isolable formylsilane $(Me_3Si)_3SiCHO$ (eq 9). The reaction chemistry of this new chemical species has been briefly examined.[25]

$$CpCp^*Zr[\eta^2\text{-}COSi(SiMe_3)_3]Cl \xrightarrow[-78°C]{HCl} CpCp^*ZrCl_2 + (Me_3Si)_3Si\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}H \quad (9)$$

Early metal silaacyl complexes may also function as precursors to acylsilanes (R_3SiCOR'), useful synthetic intermediates for which few synthetic routes exist. In sterically congested silaacyl/alkyl complexes, such as $Cp^*_2Zr[\eta^2\text{-}COSiHMes_2]Me$ and $CpCp^*Zr[\eta^2\text{-}COSi(SiMe_3)_3]Me$, clean isomerizations readily take place to afford the hydrido, silyl-substituted enolates $Cp^*_2Zr[OC(=CH_2)SiHMes_2]H^7$ and $CpCp^*Zr[OC(=CH_2)Si(SiMe_3)_3]H,^{26}$ respectively. These reactions are believed to involve carbon-carbon coupling to give intermediate acylsilane complexes that undergo β-H elimination to yield the enolates (eq 10). Treatment of the enolate
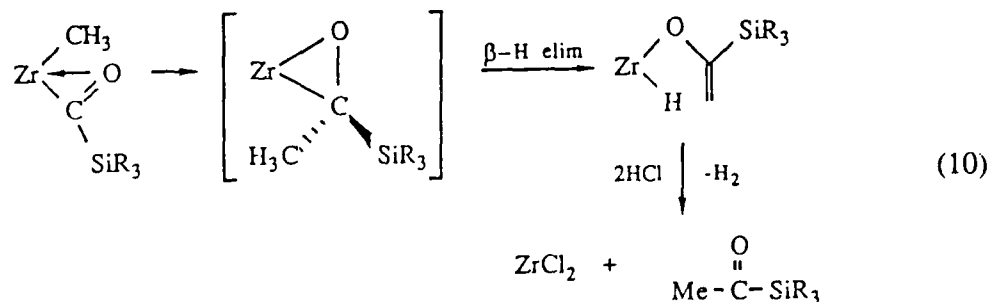
complexes with 2 equiv of HCl gives high yields of acysilanes.[26] These reactions therefore represent a new, Zr-mediated acylsilane synthesis from silyl lithiums, CO and Grignard reagents.

<u>CO/CO Coupling Reactions; Facile Ether-Cleavage</u>. Our investigations into the synthetic potential of silaacyl ligands has proven most fruitful with the reactive tantalum compound $Cp^*Cl_3Ta(\eta^2\text{-}COSiMe_3)$ (**21**), which serves as a well-behaved system that has been used to learn more about the fundamental characteristics of η^2-acyls. Compound **21** undergoes a carbon-carbon

bond-forming reaction with CO to produce a reactive ketene intermediate, $Cp^*Cl_3Ta[O(Me_3Si)C=C=O]$, which is highly electrophilic. Ethers containing β-hydrogens undergo remarkably facile cleavages upon reaction with this intermediate; with diethyl ether the alkoxy ester $Cp^*Cl_3TaOCH(SiMe_3)C(O)OEt$ and ethylene are formed.[27] The intermediate ketene can also be trapped by PCy_3 to give the crystallographically characterized $Cp^*Cl_3TaOC(=PCy_3)C(O)SiMe_3$. These unusual reactions, which appear to require the presence of the silyl group, have been studied in detail, and are the subject of a full paper.[28]

Tetrahedral Lewis Base Adducts of an Acyl. It has become clear that $Cp^*Cl_3Ta(\eta^2\text{-}COSiMe_3)$ (21) is an exceptionally electrophilic carbonyl compound, which undergoes a number of unprecedented reactions. Addition of amines and phosphines to 21 results in formation of stable adducts in which the Lewis donor is bound to the carbonyl carbon (eq 11, L = pyridine,

$$\text{(11)}$$

PMe_3, PEt_3, $P(OMe)_3$), rather than to the formally 16-electron Ta center. X-ray structures of the pyridine (Figure 4) and PEt_3 adducts have been determined. These stable compounds are the first
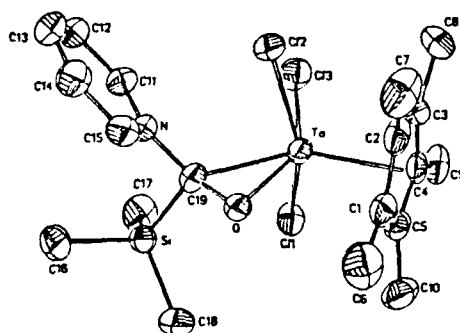
Figure 4. ORTEP view of $Cp^*Cl_3Ta[\eta^2\text{-}OC(SiMe_3)(pyr)]$.

of their type arising from addition of a neutral donor to a carbonyl compound. They provide evidence for the formation of tetrahedral intermediates in the reactions of η^2-acyls, and establish a new structural type to be considered as an intermediate in acyl-coupling processes. They also serve as models for tetrahedral intermediates in organic acyl substitution reactions, for which much

research effort has been dedicated. Tetrahedral amine adducts are thought to take part in nucleophilic acyl substitution reactions, such as the pyridine-catalyzed hydrolysis of anhydrides.[29]

The trimethyl phosphite complex $Cp^*Cl_3Ta[\eta^2-OC(SiMe_3)P(OMe)_3]$ undergoes a spontaneous Arbuzov-like dealkylation to MeCl and $Cp^*Cl_2Ta[\eta^4-OC(SiMe_3)P(OMe)_2O]$. The latter compound contains the unusual η^4-phosphonatosilaccyl(2-) ligand.[30] Silaacyl 21 reacts rapidly with diphenyldiazomethane to provide the first example of a reaction between an η^2-acyl and a diazoalkane (eq 12). The product 22, characterized by X-ray crystallography, is a silaacyl

$$(12)$$
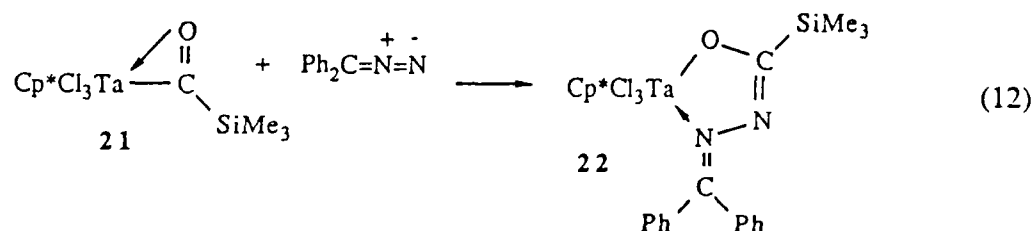
adduct in which the M-C acyl bond has been cleaved.[31]

<u>Reactions of Silaacyl Ligands with Pyridine</u>. Phosphine adducts $Cp^*Cl_3Ta[\eta^2-OC(SiMe_3)(PR_3)]$ react with pyridine according to eq 13. This process formally involves insertion
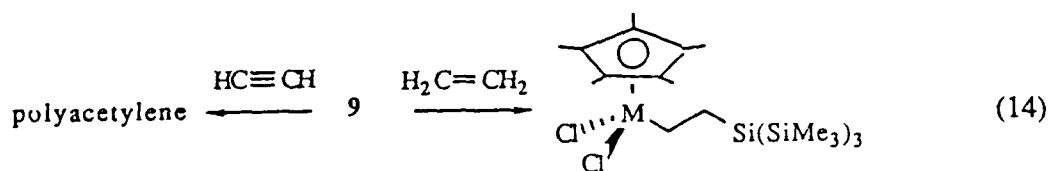

$$(13)$$
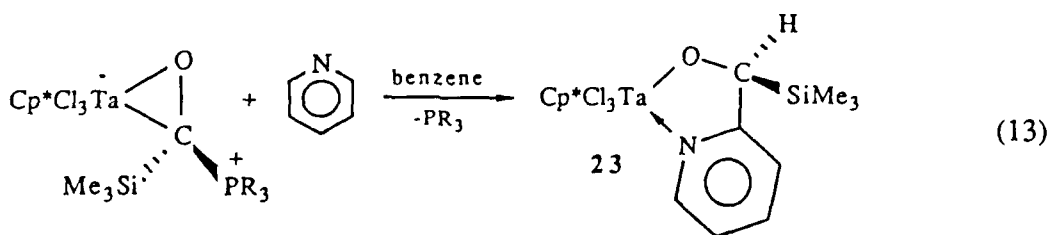
of the silaacyl carbon atom into an *ortho* C-H bond of pyridine, and is believed to proceed through an intermediate η^2-silaacyl/pyridine complex.[28] Further support for this has been found in studies of the direct reaction between $Cp^*Cl_2Hf[\eta^2-COSi(SiMe_3)_3]$ and pyridine to give a product analogous to 23 with extremely high diastereoselectivity (>99%).[32] Mechanistic studies have been carried out on both the tantalum and hafnium systems.

<u>Insertion of Organic Carbonyls into a Ta-Si bond</u>. In cases where insertion of an organic carbonyl into a transition-metal-silicon bond has been previously observed, the reactions proceed by Si-O bond formation to give α-siloxyalkyl derivatives, M-CRR′(OSiR″$_3$). In contrast

aldehydes and ketones react with the tantalum silyl $Cp^*Cl_3TaSiMe_3$ to give α-silylalkoxides $Cp^*Cl_3TaOCRR'(SiMe_3)$, and the first examples of nucleophilic transfer of a silyl group from a transition-metal to a carbonyl functionality. The reactions obey clean second-order kinetics, with the rates being highly dependent on the nature of the carbonyl substituents. These results reveal the potential for using transition-metal silyl complexes to achieve chemoselective nucleophilic transfer of silyl groups to unsaturated substrates. It seems likely that this synthetic method can be refined to provide a range of stereoselective silyl additions.[33]
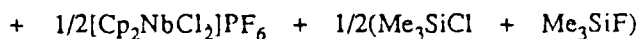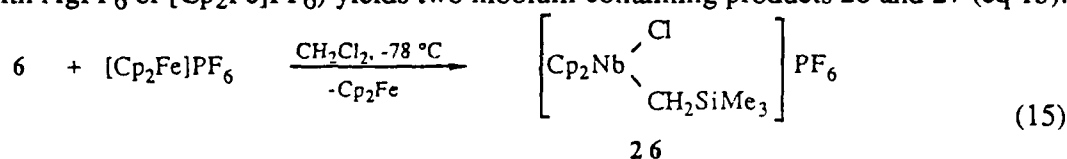
Other Insertion Reactions with M-Si Bonds. Numerous unsaturated molecules are catalytically or stoichiometrically reduced by transition-metal-silane systems. The degree to which insertions into M-Si bonds contribute to this reactivity is unclear, since very few insertions involving M-Si bonds have been directly observed. The early-transition-metal silicon systems that we have developed are much more reactive toward insertion reactions than previously studied cases, and have allowed us to carry out and study a number of insertion reactions for the first time. It appears that overall, the insertion chemistry associated with these new M-Si bonds is comparable to, and in some cases greater than, analogous M-C bonds. Other examples of insertions include reactions between isocyanides and zirconium silyls to give products such as $Cp_2Zr[\eta^2\text{-}C(Nxyl)Si(SiMe_3)_3]Cl$,[11] and insertion of N_2CPh_2 into the Ta-Si bond of $Cp^*Cl_3TaSiMe_3$, affording $Cp^*Cl_3Ta[\eta^2\text{-}N(SiMe_3)N=CPh_2]$.[33]

Insertions of olefins and acetylenes into M-Si bonds are of interest, since such reactions could be useful methods for introducing silyl substitution into organic compounds. Also, it now appears as though such insertion chemistry may be highly relevant to the mechanism of catalytic hydrosilation.[34] We had hoped that early metal silyls could be used in this manner, just as the hydride $[Cp_2ZrHCl]_n$ can be used to introduce functionality via additions to olefins or acetylenes (hydrozirconation).[35] Most early-transition-metal silyls that we have discovered do not react with carbon-carbon multiple bonds. However, recently we have discovered the first "silylzirconation" reactions; the compounds $CpCp^*Zr[Si(SiMe_3)_3]Cl$ (24) and $Cp^*Cl_2MSi(SiMe_3)_3$ (9, M = Zr; 10, M = Hf) add to ethylene to afford β-silyl alkyl complexes (e.g., eq 14).[16] These reactions proceed

$$\text{polyacetylene} \xleftarrow{\quad HC\equiv CH \quad} \mathbf{9} \xrightarrow{\quad H_2C=CH_2 \quad} \underset{Cl}{\overset{Cl'''}{\underset{Cl}{\diagup}}}M\diagdown Si(SiMe_3)_3 \qquad (14)$$

at reasonable rates in the presence of room light, and appear to follow both thermal and photochemical pathways. Compounds **9** and **10** are efficient acetylene polymerization catalysts. The scandium silyl $Cp_2Sc[Si(SiMe_3)_3](THF)$ (**12**) reacts with ethylene to produce high molecular weight polyethylene ($M_n = 75,000$), apparently because in this case the initially formed β-silyl alkyl complex is also reactive toward ethylene insertion.[14]

Oxidation Chemistry of $Cp_2Nb(SiMe_3)Cl$. Attempts to chemically oxidize $Cp_2Nb(SiMe_3)Cl$ (**6**) to a niobium(V) silyl compound led only to uncharacterized mixtures of paramagnetic solids, unless the reaction was carried out in dichloromethane. Oxidation of **6** in CH_2Cl_2 (with $AgPF_6$ or $[Cp_2Fe]PF_6$) yields two niobium-containing products **26** and **27** (eq 15).

$$\mathbf{6} \quad + \quad [Cp_2Fe]PF_6 \quad \xrightarrow[\text{-Cp}_2\text{Fe}]{CH_2Cl_2, \text{-78 °C}} \quad \left[Cp_2Nb\underset{CH_2SiMe_3}{\overset{Cl}{\diagdown}} \right] PF_6 \qquad (15)$$

$$\mathbf{26}$$

$$+ \quad 1/2[Cp_2NbCl_2]PF_6 \quad + \quad 1/2(Me_3SiCl \quad + \quad Me_3SiF)$$

$$\mathbf{27}$$

Compound **26** was characterized by X-ray crystallography. The source of the methylene unit in **26** is the dichloromethane solvent, as determined by deuterium-labeling. Mechanistic studies suggest that this reaction involves oxidative addition of CH_2Cl_2 to $[Cp_2Nb]PF_6$, which is produced by an oxidatively-induced elimination of Me_3SiCl from **6**. Our investigations of niobocene silyl chemistry have allowed us to examine silyl derivatives of Nb(III), Nb(IV), and (presumably) Nb(V). Within these systems, our results point toward a general ordering of reactivity with respect to niobium oxidation state and electron count of: Nb(V), 16 electron > Nb(IV), 17 electron > Nb(III), 18 electron.[10]

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Work from this grant has so far resulted in the following publications:

1. "Ether Cleavage Following Insertion of Carbon Monoxide into the Tantalum-Silicon Bond of $(\eta^5\text{-}C_5Me_5)Ta(SiMe_3)Cl_3$." J. Arnold and T. D. Tilley. *J. Am. Chem. Soc.* **1985**, *107*, 6409.

2. "Tetrahedral Lewis Base Adducts of an Acyl. Preparation and X-ray Structure of the Pyridine Adduct $(\eta^5\text{-}C_5Me_5)Cl_3Ta[\eta^2\text{-}OC(SiMe_3)(NC_5H_5)]$." J. Arnold, T. D. Tilley and A. L. Rheingold. *J. Am. Chem. Soc.* **1986**, *108*, 5355.

3. "Preparation and Reaction Chemistry of Trimethylsilyl Derivatives of Tantalum. X-ray Structures of d^0 $(\eta^5\text{-}C_5Me_5)Ta(SiMe_3)Cl_3$ and d^1 $(\eta^5\text{-}C_5Me_5)Ta(SiMe_3)(PMe_3)Cl_2$." J. Arnold, D. N. Shina, T. D. Tilley and A. M. Arif. *Organometallics* **1986**, *5*, 2037.

4. "Coordinatively Unsaturated Tris(trimethylsilyl)silyl Complexes of Chromium, Manganese and Iron." D. M. Roddick, T. D. Tilley, A. L. Rheingold and S. J. Geib. *J. Am. Chem. Soc.* **1987**, *109*, 945.

5. "Preparation and Reaction Chemistry of Trimethylsilyl Derivatives of Niobium. Redox Chemistry of $(\eta^5\text{-}C_5H_5)_2Nb(SiMe_3)Cl$ and X-ray Structures of $(\eta^5\text{-}C_5H_5)_2Nb(SiMe_3)(\eta^2\text{-}C_2H_4)$ and $[(\eta^5\text{-}C_5H_5)_2Nb(CH_2SiMe_3)Cl]PF_6$." J. Arnold, T. D. Tilley, A. L. Rheingold and S. J. Geib. *Organometallics* **1987**, *6*, 473.

6. "Reactions of Carbon Monoxide with Trimethylsilyl and Tris(trimethylsilyl)silyl Derivatives of Group 4 Metals. Synthesis, Characterization, and Reactivity of Silaacyl Complexes." B. K. Campion, J. Falk and T. D. Tilley. *J. Am. Chem. Soc.* **1987**, *109*, 2049.

7. "Insertion of Organic Carbonyls into the Tantalum-Silicon Bond of $(\eta^5\text{-}C_5Me_5)Cl_3TaSiMe_3$. Preparation and Characterization of the α-Silylalkoxides $(\eta^5\text{-}C_5Me_5)Cl_3TaOCRR'SiMe_3$." J. Arnold and T. D. Tilley. *J. Am. Chem. Soc.* **1987**, *109*, 3318.

8. "Formation of the Novel Benzophenone Sila-acylhydrazonato Complex $(\eta^5\text{-}C_5Me_5)Cl_3Ta\text{-}[OC(SiMe_3)NNCPh_2]$ Following Addition of Diphenyldiazomethane to an $\eta^2\text{-}Sila\text{-}acyl$ Ligand." J. Arnold, T. D. Tilley, A. L. Rheingold and S. J. Geib. *J. Chem. Soc., Chem. Commun.* **1987**, 793.

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